5th WORLD SURFACTANTS CONGRESS

May 29 - June 2, 2000
Fortezza da Basso
Firenze

FIRENZE 2000

PROCEEDINGS
Volume 2

CESIO

Comité Européen
des Agents de Surface

FEDERCHIMICA
Assobase - P.I.T.I.O.

Produttori Italiani
di Tensioattivi

SOLUTION AND PERFORMANCE PROPERTIES OF
NEW BIODEGRADABLE HIGH-SOLUBILITY SURFACTANTS

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Abstract

Phase behavior, surface activity, and cleaning performance of biodegradable anionic and nonionic surfactant derivatives of long-chain alcohols have been studied. A tailored hydrophobe structure, which can be obtained through selective skeletal-isomerization of linear olefins followed by hydroformylation, provides enhanced cold-water solubility and improved water hardness tolerance as compared to conventional predominantly linear alcohol sulfates of comparable molecular weight. The impact of the structure on ethoxylated nonionic surfactant properties is less pronounced, although differences in physical properties such as pour point and gel formation are noted when compared to linear alcohol ethoxylates. Results of radiotracer detergency studies performed in a Terg-O-Tometer confirm the positive attributes of the high-solubility surfactants. This class of surfactant may permit advances in the consumer laundry process viewed from a full lifecycle perspective by enabling high cleaning performance under conditions favoring an improved environmental profile.

Résumé

Le comportement de phases, l'activité de surface et le pouvoir nettoyant des dérivés tensioactifs anioniques et non ioniques ont fait l'objet d'une étude. Une structure hydrophobe spécialement adaptée, qui peut être obtenue par l'intermédiaire de l'isomérisation squelettique des oléfines linéaires, suivie de l'hydroformylation, fournit une plus grande solubilité par temps froid et une meilleure tolérance de la dureté de l'eau, par rapport aux sulfates d'alcool conventionnels principalement linéaires dont le poids moléculaire est comparable. L'impact de la structure sur les propriétés des agents tensioactifs non ioniques éthoxylés est moins marqué, bien que des différences soient observées dans les propriétés physiques, telles que le point d'écoulement et la formation de gel, par rapport aux éthoxylats d'alcool linéaire. Les résultats des études de détergence au traceur radioactif effectuées dans un "Terg-O-Tometer" confirment les attributs positifs des agents tensioactifs de haute solubilité. Cette classe d'agents tensioactifs pourrait permettre de faire des progrès au niveau du processus de blanchissage de consommation, si on le considère du point de vue d'un cycle de vie complet, sous des conditions qui favorisent un meilleur profil environnemental.

Zusammenfassung

Es wurden Phasenverhalten, Grenzflächenaktivität und Reinigungsleistung biologisch zersetzbarer anionischer und nichtionisierender Tensidderivate untersucht. Eine genau abgestimmte wasserabweisende Struktur, die durch eine besonders gewählte Skelett-Isomerisierung linearer Olefins und einer nachfolgenden Hydroformylierung gebildet wurde, bietet eine erhöhte Kaltwasserlöslichkeit und bessere Wasserhärtetoleranz als herkömmliche und meistens lineare Alkoholsulfate eines vergleichbaren Molekulargewichts. Der Struktureinfluß auf die Eigenschaften ethoxylierter nichtionisierender Tenside ist weniger ausgeprägt, obwohl Unterschiede in den physikalischen Eigenschaften wie Pourpoint und Gelbildung im Vergleich mit linearen Alkoholethoxylaten zum Vorschein kommen. Mit den Ergebnissen von Radionuklid-Untersuchungen in einem Torg-O-Tometer wurden die positiven Merkmale der Tenside mit hoher Löslichkeit bestätigt. Aus der Sicht einer Voll-Lebenskreislauf-Perspektive unter Bedingungen, die ein verbessertes Umweltprofil begünstigen, kann diese Tensidgruppe zu einem Fortschritt des Verbraucher-Wäschereiprozesses führen.

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INTRODUCTION

Branched alcohols are an important constituent of many high volume synthetic detergent alcohols made using the Oxo process (1). In separate work, it was shown that the separated branched fraction of certain synthetic alcohols exhibited an excellent biodegradation profile (2). It was obviously of interest to document the effect of specific alcohol branching on the surfactant properties of alcohol sulfates. Additionally, random mono-methyl alcohols were synthesized, and physical chemistry and laboratory cleaning evaluations conducted.

Early German workers used laboratory organic synthesis to make a limited series of alcohols and sulfates (3). For this research, two versatile synthetic schemes were adapted to a wide range of compounds, and the performance testing was likewise modified to reflect current practice including lower wash temperatures.

EXPERIMENTAL

General Methods for Synthesis: As depicted in Figure 1, a variety of alcohols were synthesized by

Figure 1

Malonic Ester Synthesis of 2-Alkyl Branched Alcohols
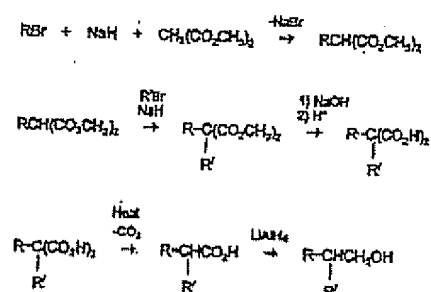
alkylation of malonic ester (4). With this method, alcohols with a total of C-12 to C-18 were made, and 2-alkyl branches from C-1 to C-6 were incorporated. Figure 2 shows the two-step procedure for introducing random mono-methyl branching into an alcohol (5). The alcohols were > 97% pure. All alcohols were converted to alcohol sulfate sodium salts according to the published procedure with ClSO$_3$H, followed by neutralization with NaOH (6).

Figure 2

Random Methyl Alcohol Synthesis
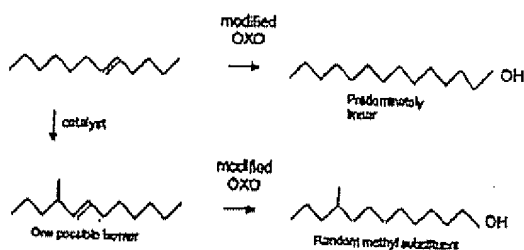
Krafft Temperatures of Alcohol Sulfates: Aqueous 1% surfactant solutions were frozen, and the solutions were allowed to slowly warm. The reported Krafft temperature is the temperature where the solution was fully transparent.

Calcium Tolerance: Aqueous surfactant solutions were made at a concentration of 0.06% weight, and adjusted to a pH of approximately 9 with 1% NaOH. The surfactant solutions were warmed to 40 °C. Aliquots of 10% $CaCl_2$ were added, and the surfactant which remained dissolved in the upper (clear) layer was determined via the two phase titration method (7). The reported calcium tolerance is amount of $CaCl_2$ which must be added to precipitate 50% of the anionic surfactant.

The random mono-methyl C-16,17 alcohol was ethoxylated with an average of nine ethylene oxide groups using standard KOH ethoxylation. For comparison, a nine-EO ethoxylate with a linear C-16 hydrophobe was prepared by blending ethoxylates obtained from Uniqema. Also studied were the seven-EO ethoxylates obtained through standard ethoxylation of the linear and branched fractions of a predominately linear C-14,15 alcohol.

The cloud point and Krafft temperature of 1% aqueous alcohol ethoxylate solutions were measured in deionized water using dipping probe turbidimetry (8,9). Solutions were first chilled overnight in a freezer at -5°C. The solutions were then heated at a rate of about 1°C/minute in a jacketed beaker with agitation provided by a Glas-Col® non-aerating stirrer at 3000 rpm. Turbidity was determined by measuring the light transmittance through the solution at 650 nm. The first temperature where complete clearing of the solution occurred was taken as the Krafft temperature while the higher temperature at which turbidity reappeared due to formation of a dispersed phase was taken as the cloud point.

Solution Time Method: The solution times of the neat ethoxylates were measured by injecting 0.20 cc of liquid surfactant into 50 cc deionized water in a flat bottom pour point tube (Corning No. 6900). The water was stirred at 500 rpm with a 1.5 cm x 0.5 cm magnetic stirring bar. The times for complete surfactant dissolution were measured at 25°C with the temperature of the sample being controlled by placing the pour point tube in a thermostatically-controlled water bath. Measurements were performed in duplicate and averaged.

Alcohol Ethoxylate Pour Points: Pour points for the commercial C-14,15 samples were obtained using method ASTM D97-85 with an automatic pour point apparatus. Visual determination of pour points was made for the other samples by observing their flow behavior as 50 cc were slowly warmed in a water bath.

Surface Tension: Equilibrium surface tension as a function of surfactant concentration was measured at 25°C using an automated Lauda tensiometer. This instrument doses fixed increments of stock solution into 100 cc of deionized water that is contained in a thermostatically-controlled beaker. Equilibrium surface tension is measured automatically using the Du Nuoy ring method. From the surface tension-concentration plots, critical micelle concentration was determined by standard procedures (10).

Detergency: Multisebum soil removal was determined using the published laboratory radiotracer detergency procedure (11,12). All alcohol sulfates were evaluated in the following prototype formulation: 0.2 g/L anionic, 0.34 g/L zeolite, and 0.2 g/l of Na_2CO_3.

Biodegradation: A laboratory estimation of biodegradation was conducted by an adaptation of the CO_2 evolution method of Sturm (13)

DISCUSSION

- Biodegradation

A screening study of biodegradation was used to compare a variety of alcohol sulfates. As depicted in Figure 3, only a surfactant synthesized to contain a quaternary carbon atom failed to evolve CO_2 at a

Figure 3
Closed Bottle Biodegradation Results for 2-Alkyl Alcohol Sulfates
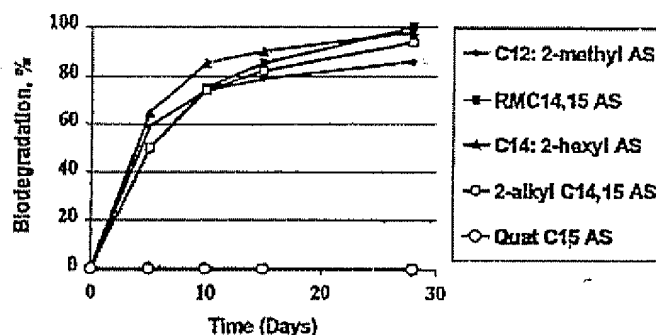

rapid rate.. A variety of 2-alkyl branches or a random mono-methyl substituent all preformed equally well in this screen. This result was at least in part predicted by the previous work from Shell (2).

- Surfactant Properties of 2-Alkyl Alcohol Sulfates

Displayed in Figure 4 are the Krafft temperatures of branched C-16 alcohol sulfates. With this series of alcohol sulfates, the minimum in Krafft temperature occurs with the attachment of a 2-butyl group. The all linear hexadecanol sulfate has a Krafft temperature of 45 °C (14).

Figure 4
Krafft Temperature of C16: 2-Alkyl Branched Alcohol Sulfates
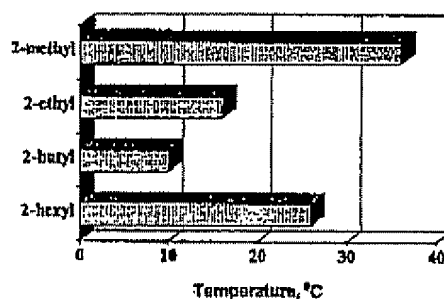
The calcium tolerance of this series of C-16 alcohol sulfates is depicted in Figure 5. The methyl and ethyl derivatives are approximately equal, while either butyl or hexyl introduce the greatest solubility.

Calcium Tolerance of C16; 2-Alkyl Alcohol Sulfates

2-methyl
2-ethyl
2-butyl
2-hexyl
Br. E C1415

0   100   200   300   400   500   600

$CaCl_2$, ppm
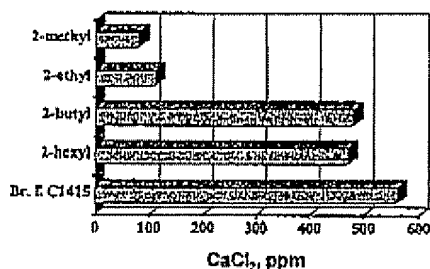
· • Detergency Evaluation of 2-Alkyl Alcohol Sulfates

In 1969 Götte and Schwuger (3) reported the reflectance detergency of branched C-16 alcohol sulfates at 40 °C. It was noted that the 2-methyl branched alcohol sulfate gave the highest level of cleaning. With the availability of a broader selection of chain lengths, the generality of this observation has been investigated.

In this present work, C-16 alcohol sulfates were evaluated at 10 °C by an alternative radiotracer

Figure 6
Multisebum Detergency of C16 Alcohol Sulfates: 10 °C and 150 ppm Water Hardness

2-methyl
1-ethyl
2-butyl
2-hexyl

0   5   10   15   20

%Soil Removal, LSD_{95} = 4
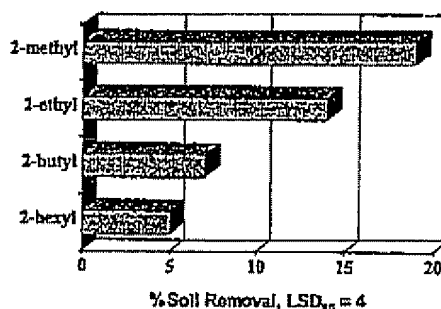
method, see Figure 6. Despite having the highest Krafft temperature and the lowest calcium tolerance, the 2-methyl derivative is the best performer, as observed by Götte and Schwuger (3). It is remarkable that the pattern was the same, since the temperature, soil, builder, and formulation are all different. This excellent activity is probably the result of greater surface activity of the 2-methyl surfactant. However, it is likely that the surfactant did not fully dissolve at the detergency conditions used here.

Additionally, a variety of total chain lengths, all with 2-methyl branches were evaluated, Figure 7. Performance is optimized for the C-16 total chain length, at the low temperature cleaning conditions utilized. It is presumed that the C-12 derivative has a relatively high cmc, and thus more surfactant would have been required. The C-18 material was poorly soluble, and therefore little surfactant was available at the conditions of this evaluation.

These surface chemistry and cleaning studies suggested that the length of the branch was an important variable in hydrophobe optimization. Exploratory chemistry yielded a way to synthesize alcohols with nearly exclusively methyl substituents (5).

Figure 7

Detergency Performance of 2-Methyl Branched Alcohol Sulfates
10 °C and 150 ppm Hardness

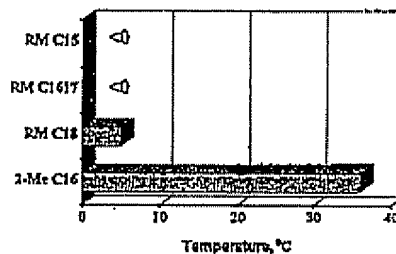% Soil Removal, LSD$_{85}$=4
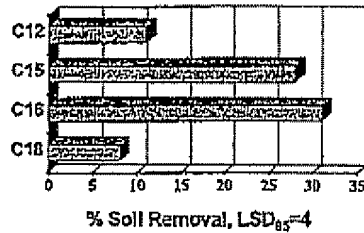
- Surfactant Properties of Random Methyl Alcohol Sulfates

Shown in Figures 8 and 9 are surfactant properties as a function of carbon content for the random methyl branched alcohol sulfates. Excellent cold water solubility is exhibited by all three RM samples

Figure 8

Krafft Temperature of RM Branched Alcohol Sulfates

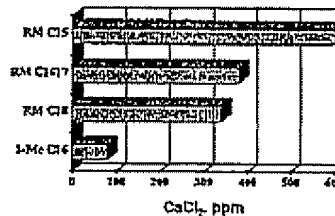Temperature, °C

better Solubility than C2 branched only

as compared to pure 2-Me C16 alcohol sulfate which is not fully soluble at 1% concentration until heated to 36°C. Also, as shown in Figure 9, the random methyl systems exhibit much higher calcium tolerance than the 2-Me C16 alcohol sulfate.

Figure 9
Calcium Tolerance of RM Branched Alcohol Sulfates

CaCl$_2$, ppm

Critical micelle concentration values in deionized water for the RM sulfates at 25°C are compared in Figure 10 to values for a predominantly linear C1415 alcohol sulfate and C12 LAS. As expected, the RM alcohol sulfates having a high molecular weight exhibit quite low cmc's, indicative of low dosing requirements in laundry processes. Nevertheless, their Krafft temperatures are much lower than that for the commercial C1415 linear alcohol sulfate (37°C), and their calcium tolerance is much higher than

those for the C1415 sulfate and C12LAS, which are 40 ppm and 140 ppm, respectively. All three

Figure 10

Critical Micelle Concentration of RM
Branched Alcohol Sulfates


Surfactant Concentration, ppm
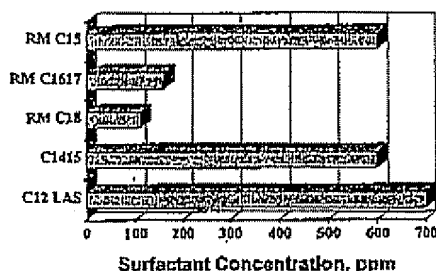
factors, low Krafft temperature, high calcium tolerance, and low cmc, are positive attributes of the random methyl alcohol sulfates which should contribute to excellent detergent properties, particularly in underbuilt systems at low washing temperatures.

- Detergency Evaluation of Random Methyl Alcohol Sulfates

Three different random-methyl alcohol sulfates were compared to a linear C-14,15 alcohol sulfate, Figure 11. Each of the randomly substituted alcohol sulfates was superior to the comparison surfactant.

Figure 11

Detergency Performance of RM Branched
Alcohol Sulfates
10 °C and 150 ppm Hardness
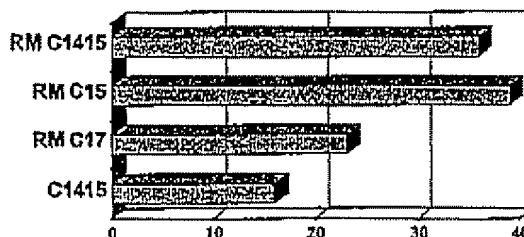
better detergency

Random Methyl and 2-Alkyl Ethoxylates

Shown in Table 1 are the results for the tested ethoxylates. For a given average hydrophobe weight, the presence of branching resulted in modest reductions in pour point and an increase in critical micelle concentration. Interestingly, a Krafft temperature phenomenon was noted in the linear systems which is atypical for nonionic surfactant systems. These systems exhibit decreased solubility both at low temperatures due to crystallinity and at high temperatures where EO dehydration results in phase separation above the cloud point temperature. In contrast, no crystallization occurred at 1% concentration for the branched analogues, i.e., the Krafft temperatures for these systems were below zero. The lower solubility in cold water exhibited by the linear ethoxylates also contributes to the much slower rates of dissolution observed for these systems at 25°C as compared to the respective branched ethoxylates.

Table 1

Physical and Solution Properties of Branched
and Linear Alcohol Ethoxylates

Surfactant	Pour Point (°C)	Cloud Point (°C)	Krafft Temperature (°C)	Dissolution Time (min.)	Critical Micelle Concentration (ppm)
C14,15-7 (linear)	24	50	25	21	3
2-alkyl C14,15-7	19	a)	20	8	8
C13-9 (linear)	22	65	35	>120	1
RM C16,17-9	21	50	20	32	4

a) solution was slightly turbid between 0 and 40°C resulting in no distinct cloud point

CONCLUSIONS

The surfactant properties and detergency performance of model 2-alkyl alcohol sulfates have been examined. Addition of a 2-alkyl group reduces the Krafft temperature, improves the calcium tolerance, and the surfactants biodegrade readily.

Additionally:

- laboratory synthesis methods have been developed to prepare random mono-methyl alcohols, which are readily converted to either sulfates or ethoxylates;

- both specific 2-alkyl and random mono-methyl substituents improve the physical chemistry properties of the corresponding alcohol sulfates;

- solubility enhancements are likewise observed for alcohol ethoxylates containing the same branched hydrophobes; and,

- both 2-alkyl branched alcohol sulfates and random mono-methyl sulfates clean well, particularly at cool wash temperatures.

It is expected that a full environmental profile for random methyl substituted surfactants would be favorable: excellent biodegradation is expected, and the combination of good solubility and low sensitivity to water hardness should translate into the ability to wash at lower water temperatures.

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